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The first ring-enlargement of a 1-Azabicyclo[1.1.0]butane to a 1-Azabicyclo[2.1.1]hexane

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Abstract: The reactions of 3-phenyl-1-azabicyclo[1.1.0]butane (4) with dimethyl dicyanofumarate ((E)-8) and dimethyl dicyanomaleate ((Z)-8) lead to the same mixture of cis- and trans-4-phenyl-1-azabicyclo[2.1.1]hexane 2,3-dicarboxylates (cis-11 and trans-11, resp.; Scheme 3). This result of a formal cycloaddition to the central C-N bond of 4 is interpreted by a stepwise reaction mechanism via a relatively stable zwitterionic intermediate 10, which could be intercepted by morpholine to give a 1 : 1 : 1 adduct 12, which undergoes a spontaneous elimination of HCN to yield the fumarate 13 (Scheme 4).

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The First Ring-Expansion of a 1-Azabicyclo[1.1.0]butane to a 1-Azabicyclo[2.1.1]hexane

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The reactions of 3-phenyl-1-azabicyclo[1.1.0]butane (**4**) with dimethyl dicyanofumarate ((*E*)-**8**) and dimethyl dicyanomaleate ((*Z*)-**8**), respectively, lead to the same mixture of *cis*- and *trans*-4-phenyl-1-azabicyclo[2.1.1]hexane 2,3-dicarboxylates (*cis*- and *trans*-**11**, *Scheme 3*). This result of a formal cycloaddition to the central N,C-bond of **4** is interpreted by a stepwise reaction mechanism *via* a relatively stable zwitterionic intermediate **10**, which could be intercepted by morpholine to give a 1:1:1 adduct **12**, which undergoes a spontaneous elimination of HCN to yield the fumarate **13** (*Scheme 4*).

1. Introduction. – Strained bicyclo[1.1.0]butane derivatives are attractive compounds for theoretical and spectroscopic studies [1]. As soon as the first example had been synthesized [2], numerous reports appeared in which differently substituted representatives were explored as useful building blocks for the preparation of cyclobutanes and cyclobutenes [3], as well as larger bicyclic systems. One of the first observations was the ring enlargement to give a bicyclo[2.1.1]hexane *via* a formal cycloaddition with differently substituted ethenes [4]. It turned out that in the case of 3-methylbicyclo[1.1.0]butane carbonitrile (**1**), the reactions with electron-rich olefins, *e.g.* (cyclopenten-1-yl)-*N,N*-dimethylamine, led to the polycyclic adduct **2** in high yield [4] (*Scheme 1*). On the other hand, the electron-deficient 2,2-bis(trifluoromethyl)ethene-1,1-dicarbonitrile (BTF) afforded the cyclobutene derivative **3** [3]. These reactions are believed to occur stepwise *via* diradical intermediates.

Scheme 1

In comparison with bicyclo[1.1.0]butanes, the relatively stable 1-aza-analogues¹⁾ are rarely applied as starting materials for the synthesis of N-heterocycles. The main products obtained are azetidines, which are smoothly formed when 1-azabicyclo[1.1.0]butanes are treated with electrophilic reagents. For example, 3-phenylazabicyclo[1.1.0]butane (**4**) adds alkyl chloroformates at room temperature in a fast reaction to give 3-chloro-3-phenylazetidine-1-carboxylates of type **5** [6] (*Scheme 2*). A recent report described the smooth addition of hydrazoic acid across the 1,3-bond to produce **6** [7]. The electrophilic

¹⁾ The first synthesis of 1-azabicyclo[1.1.0]butanes, the parent system, as well as the 3-methyl and 3-ethyl derivatives, was reported in 1969 [5].

dichlorocarbene reacts with **4** under ring opening to give the 1,1-dichloro-2-azapenta-1,4-diene **7** [8]²). Similar results were obtained with (chloro)(phenyl)carbene and 3-ethyl-1-azabicyclo[1.1.0]butane [10].

Scheme 2

To the best of our knowledge, there are no reports on the reaction of 1-azabicyclo[1.1.0]butanes with alkenes to give cycloadducts or other adducts corresponding with the reactions depicted in *Scheme 1*. The present paper focusses on preliminary results obtained from the reactions of **4** with electron-deficient alkenes,

2. Results and Discussion. – In analogy to other bicyclic tertiary amines, 1-azabicyclo[1.1.0]butanes are expected to be basic³ and nucleophilic substances. For this reason, electron-deficient alkenes should readily undergo reactions with 1-azabicyclo[1.1.0]butanes. The first experiment carried out with **4** and BTF in CH₂Cl₂ at 0-5° showed that an exothermic reaction occurs. The product obtained thereby was a thick, colorless oil with all characteristics of a polymeric material. A similar reaction course of the reaction was observed in the case of ethenetetracarbonitrile (TCNE). However, when a solution of 1 equiv. of **4** in CH₂Cl₂ was added dropwise to a suspension of 3 equiv. of

²) All attempts to add the nucleophilic dimethoxycarbene to **4** were in vain and **4** was recovered almost quantitatively [9].

³) As far as we know, no physicochemical studies on the basicity of 1-azabicyclo[1.1.0]butanes have been reported.

dimethyl dicyanofumarate (DCFM, (*E*)-**8**) in CH₂Cl₂, the suspension dissolved slowly and complete conversion of **4** was observed after 4 h.

The ¹H-NMR spectrum of the crude mixture revealed the presence of two new products with two different signals for MeO in each case. The MeO signals of the major product appear at 3.70 and 3.89 ppm and those of the minor one at 3.88 and 4.10 ppm. Based on the intensity of these signals, a ratio of *ca.* 3:1 was established for the two products. The analogous experiment with **4** and dimethyl dicyanomaleate (DCMM, (*Z*)-**8**), which was very soluble in CH₂Cl₂, led to the same mixture of products. Chromatographic separation on SiO₂-plates gave two fractions as crystalline materials, which, after recrystallization, were identified as two isomeric 1:1-adducts on the basis of their elemental analyses and mass spectra. The major isomer, with m.p. 165-167°, shows a weak IR absorption for C≡N groups at 2241cm⁻¹ and two very strong ester bands at 1777 and 1747cm⁻¹. The corresponding signals of the minor product (m.p.138-140°) appear at 2246, 1770 and 1757 cm⁻¹. In the ¹³C-NMR spectra, both isomers show signals for two non-equivalent ester-CO groups (165.5/162.3 and 164.0/162.6 ppm, resp.) and two non-equivalent C≡N groups 115.3/114.6 and 115.4/114.2 ppm, resp.). Additional characteristic signals of the major isomer are those of two CH₂ groups at 66.3 and 62.9 ppm and three signals for quaternary C-atoms at 77.9, 71.4, and 61.6 ppm. A similar set of signals was found for the minor isomer. Finally, the structure of the major product was established by X-ray crystallography (*Figure*).

Figure. *ORTEP Plot* [11] *of the molecular structure of cis-11* (arbitrary numbering of the atoms, 50 % probability ellipsoids)

The analysis proved the structure of *cis*-**11**, *i.e.* a 4-phenyl-1-azabicyclo[2.2.1]hexane with two *cis*-configured C≡N and CO₂Me groups at C(2) and C(3). Consequently, the structure of the minor product is attributed as the *trans*-isomer (*trans*-**11**).

The formation of the two isomers, *cis*- and *trans*-**11**, in the same ratio, irrespective of the use of (*E*)-**8** or (*Z*)-**8** as the reagent, can be explained by the two-step mechanism presented in *Scheme 3*. The first step of the reaction is the nucleophilic addition of **4** to the activated C=C bond in a *Michael* fashion. In the formed zwitterion **10**, the positive as well as the negative charge are ideally stabilized, which results in the prolongation of the lifetime of this species. Therefore, **10a** derived from (*E*)-**8** and **10b** derived from (*Z*)-**8** are able to equilibrate to give the same mixture. These zwitterions then undergo a cyclization by formation of a new C,C bond to yield the final products **11**. This ring closure is slow in comparison with the rotation about the C,C-bond in the zwitterions **10**.

Scheme 3

The postulated reaction pathway was additionally supported by the interception of **10** with morpholine. When the reaction of **4** and (*E*)-**8** was performed in the presence of a 5-fold excess of morpholine, the formation of a single new product was observed. The compound isolated after chromatographic workup showed in the ¹H-NMR spectrum, as well as in the IR spectrum, the presence of two different MeO₂C groups. In addition, a strong C≡N absorption appears in the IR spectrum. The ¹³C-NMR data confirmed the presence of two non-equivalent ester groups and, unexpectedly, only one signal for C≡N was detected. Based on

these data and supported by the MS and elemental analyses, the structure was elucidated as **13**, the 1:1:1 adduct after elimination of HCN (*Scheme 4*). The proposed interception product **12** could not be detected as spontaneous elimination of HCN led immediately to the isolated azetidine derivative **13**.

Scheme 4

In conclusion, the present study showed once more that zwitterions formed by nucleophilic addition to the C=C bond of (*E*)- and (*Z*)-**8** (DCFM and DCMM) are perfectly stabilized and their formation determines the pathway of the subsequent reactions. Analogous formations of intermediates have been observed in reactions of (*E*)- and (*Z*)-**8** with thiocarbonyl *S*-methanides [12], as well as with dimethoxycarbene [13]. The presented reaction with 1-azabicyclo[2.1.1]butanes opens a new and convenient access to 1-azabicyclo[2.1.1]hexanes, which are almost unknown. The only report on a synthesis of a representative of this class of 1-azabicycles concerned an alumina catalyzed rearrangement [14].

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Experimental Part

1. *General.* Melting points were determined in capillaries (*Melt-Temp. II, Aldrich*); uncorrected. IR spectra: *NEXUS FT-IR* spectrophotometer; in KBr. ^1H - and ^{13}C -NMR spectra: *Tesla BS567A* (80 and 20 MHz, resp.) or *Bruker AC 300* instrument (300 and 75.5 MHz, resp.), in CDCl_3 ; TMS as an internal standard. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instruments (CI (NH_3)).

2. *Starting Materials.* 3-Phenyl-1-azabicyclo[1.1.0]butane (**4**) was obtained from 3-phenyl-2*H*-azirine via addition of a sulfonium ylide according to [15]. Dimethyl dicyanofumarate (DCFM, (*E*)-**8**) was prepared from commercially available methyl cyanoacetate by heating in excess SOCl_2 following the protocol in [16]. Dimethyl dicyanomaleate (DCMM, (*Z*)-**8**) is conveniently available by photolysis of a DCFM solution in CH_2Cl_2 using a high pressure mercury lamp and a pyrex filter [17]. 1,1-Bis(trifluoromethyl)ethene-2,2-dicarbonitril (BTF) was prepared following the protocol in [18]. Ethenetetracarbonitrile (TCNE) was used as a commercial reagent after purification by sublimation *in vacuo*.

3. *Reactions of 4 with electron-deficient ethenes. General Procedure.* A soln. of **4** (131 mg, 1 mmol) in CH_2Cl_2 (1 ml) was dropped slowly into a stirred and cooled (water/ice bath) soln. of the appropriate ethene derivative (1 mmol) in CH_2Cl_2 (2 ml). The reactions with BTF and TCNE occurred exothermally and were complete as soon as the addition was finished. In the experiments with DCFM and DCMM, the cooling bath was removed after 1

h and stirring was continued for 4 h at r.t. After evaporation of the solvent, oily residues were analyzed by means of ^1H -NMR spectroscopy. Polymeric products obtained with BTF and TCNE were neither purified nor identified. The mixtures obtained from the reactions with DCFM and DCMM, respectively, showed identical composition with a *ca.* 3:1 ratio of two new products with characteristic ^1H -NMR signals for the MeO groups at 3.89 and 3.70 ppm for the major component and 4.08 and 3.90 ppm for the minor one. The crude mixtures were preliminarily purified on a short SiO_2 -column and subsequently separated on prep. TLC plates coated with SiO_2 by using CHCl_3 as the developing solvent. Repeated development was needed to isolate two narrowly separated fractions. The less polar fraction consisted of the minor product identified as *trans*-**11**. Analytically pure samples were obtained by recrystallization.

The reaction with DCMM was performed analogously to the procedure described for DCFM and chromatographic workup led to *trans*- and *cis*-**11** in a *ca.* 3:1 ratio.

Dimethyl cis-2,3-Dicyano-4-phenyl-1-azabicyclo[2.1.1]hexane-2,3-dicarboxylate (cis-11). More polar fraction. Yield: 120 mg (37% after PLC). Colorless crystals. M.p. 165–167° (hexane/ CH_2Cl_2). IR (KBr): 2241 vw (CN), 1777 vs (C=O), 1747 vs (C=O), 1450 m , 1443 m , 1262 vs (C–O), 1095 s , 1085 m , 1057 m , 914 m , 902 m , 840 m , 767 m , 723 m , 698 s . ^1H -NMR: 7.38–7.35(m , 3 arom. H); 7.12–7.08 (m , 2 arom. H); 3.99 (dd , $^1J = 9.4$, $^2J = 9.3$, 1 H); 3.84 (s , MeO); 3.77 (dd , $^1J = 8.0$, $^2J = 8.4$, 2 H); 3.70 (s , MeO); 3.53 (dd , $^1J = 8.9$, $^2J = 9.5$, 1 H). ^{13}C -NMR: 165.5, 162.3, (2 s , 2 C=O); 130.7 (s , 1 arom. C_q); 129.4, 129.0, 126.1 (3 d , 5 arom. CH); 115.3, 114.6 (2 s , 2 CN); 77.9 (s , C(2)); 71.4 (s , C(3)); 66.3, 62.9 (2 q , 2 MeO); 61.6 (s , C(4)); 54.5, 54.4 (2 t , 2 CH_2). CI-MS: 343 (6, $[\text{M}+\text{NH}_4]^+$), 326 (100, $[\text{M}+1]^+$). Anal. calc. for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_4$ (325.32): C 62.77, H 4.65, N 12.92; found: C 62.61, H 4.68, N 12.83.

Dimethyl trans-2,3-Dicyano-4-phenyl-1-azabicyclo[2.1.1]-hexane-2,3-dicarboxylate (trans-11). Less polar fraction. Yield: 35 mg (10 % after PLC). Colorless crystals. M.p. 138–140° (hexane/CH₂Cl₂). IR: 2246_{vw} (CN), 1770_{vs} (C=O), 1757_{vs} (C=O), 1436_m, 1270_{vs} (C–O), 1096_m, 1059_m, 750_m. ¹H-NMR: 7.41–7.33 (*m*, 3 arom. H); 7.27–7.19 (*m*, 2 arom. H); 4.08 (*s*, MeO); 3.90 (*s*, MeO); 3.92–3.87 (*m*, 2 H); 3.79–3.69 (*m*, 1 H); 3.63–3.46 (*m*, 1 H). ¹³C-NMR: 164.0, 162.6 (2_s, 2 C=O); 130.9 (*s*, 1 arom. C_q); 129.1, 128.8, 127.0 (3_d, 5 arom. CH); 115.4, 114.2 (2_s, 2 CN); 78.2 (*s*, C(2)); 68.9 (*s*, C(3)); 66.0, 64.7 (2_q, 2 MeO); 60.7 (*s*, C(4)); 55.0, 54.7 (2_t, 2 CH₂). CI-MS: 326 (100, [M+1]⁺). Anal. calc. for C₁₇H₁₅N₃O₄ (325.32): C 62.77, H 4.65, N 12.92; found: C 62.74, H 5.10, N 12.38.

4. *Reaction of 4 with (E)-8 in the presence of morpholine.* To a stirred soln. of DCFM ((*E*)-8) (194 mg, 1mmol) and morpholine (435 mg, 5mmol) in CH₂Cl₂ (1 ml), 4 (131 mg, 1 mmol) dissolved in CH₂Cl₂ (1 ml) was added drop-wise at r.t. After 5 h, the mixture was evaporated to dryness, and the evaporation was repeated 2× with small portions of toluene (2 × 5 ml) in order to remove excess morpholine. The residual thick oil was separated on TLC plates coated with SiO₂ by using CH₂Cl₂/MeOH (88.5/1.5) as the eluting system. A sole fraction with R_f ~ 0.5 was isolated and additionally purified by crystallization.

Dimethyl (E)-{2-[3-(Morpholin-4-yl)-3-phenylazetidin-1-yl]-3-cyano}but-2-enedioate (E-13). Yield: 340mg (88% after PLC). Colorless crystals. M.p. 156–158° (MeOH). IR: 2206_m (CN), 1749_s (C=O), 1702_s (C=O), 1570_{vs} (C=C), 1452_s, 1305_{vs}, 1264_{vs}, 1196_s, 1150_s, 1133_s, 1116_s, 769_w, 708_w. ¹H-NMR: 7.44–7.33 (*m*, 3 arom. H); 7.06–7.03 (*m*, 2 arom. H); 4.94, 4.91 (*AB*, *J* = 11.6, CH₂); 4.43, 4.39 (*AB*, *J* = 9.6, CH₂); 3.93 (*s*, MeO); 3.72 (*s*, MeO);

3.73–3.66 (*m*, 2 CH₂O); 2.29–2.24 (*m*, 2 CH₂N). ¹³C-NMR: 165.1, 161.8 (2 C=O); 158.2 (C(2)); 134.5 (*s*, 1 arom. C_q); 128.3, 127.1 (2*d*, 5 arom. CH); 116.9 (CN); 70.3 (C_q); 66.8 (2 CH₂O); 63.3 (C_q, C(3)); 62.6, 61.8 (2 CH₂(azetidine)); 53.7, 52.1 (2 MeO); 46.3, (2 CH₂N). CI-MS: 386 (100, [M+1]⁺), 189 (9). Anal. calcd. for C₂₀H₂₃N₃O₅ (385.41): C 62.33, H 6.01, N 10.90; found: C 62.21, H 5.94, N 10.84.

5. *X-Ray Crystal-Structure Determination of cis-11* (Table and Fig.)⁴). All measurements were performed on a *Nonius KappaCCD* area-detector diffractometer [19] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the Table, and views of the molecules are shown in the Figure. Data reduction was performed with *HKL Denzo* and *Scalepack* [20]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The structure was solved by direct methods using *SIR92* [21], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Five reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were

⁴) CCDC-287053 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via http://www.ccdc.cam.ac.uk/data_request.cif.

taken from [22a], and the scattering factors for H-atoms were taken from [23]. Anomalous dispersion effects were included in F_c [24]; the values for f' and f'' were those of [22b]. The values of the mass attenuation coefficients are those of [22c]. All calculations were performed using the *SHELXL97* [25] program.

Table. *Crystallographic Data for Compound cis-11*

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Table. *Crystallographic Data for Compound cis-11*

Crystallized from	hexane/CH ₂ Cl ₂
Empirical formula	C ₁₇ H ₁₅ N ₃ O ₄
Formula weight	325.32
Crystal color, habit	colorless, prism
Crystal dimensions [mm]	0.18 × 0.20 × 0.30
Temperature [K]	160(1)
Crystal system	triclinic
Space group	<i>P</i> [−] ,1
<i>Z</i>	2
Reflections for cell determination	4543
2 θ range for cell determination [°]	4–60
Unit cell parameters <i>a</i> [Å]	8.3240(2)
<i>b</i> [Å]	8.9030(2)
<i>c</i> [Å]	12.3691(3)
α [°]	100.752(1)
β [°]	94.808(1)
γ [°]	116.114(1)
<i>V</i> [Å ³]	794.20(3)
<i>D_x</i> [g cm ^{−3}]	1.360
μ (MoK α) [mm ^{−1}]	0.0990
Scan type	ϕ and ω
2 θ (max) [°]	60
Total reflections measured	21407
Symmetry independent reflections	4602
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3979
Reflections used in refinement	4597
Parameters refined	219
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>) reflections]	0.0416
<i>wR</i> (<i>F</i> ²) (all data)	0.1116
Weighting parameters [<i>a</i> ; <i>b</i>] ^a)	0.0507; 0.2124
Goodness of fit	1.038
Final Δ _{max} / σ	0.001
$\Delta\rho$ (max; min) [e Å ^{−3}]	0.33; -0.18

$$^a) \ w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP \text{ where } P = (F_o^2 + 2F_c^2)/3$$

Legends

Figure. *ORTEP Plot* [11] of the molecular structure of *cis*-**11** (arbitrary numbering of the atoms, 50% probability ellipsoids)